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(54) METHOD FOR PRODUCING MOLDED FOAM ARTICLES, AND MOLDED FOAM ARTICLES

VERFAHREN ZUR HERSTELLUNG VON SCHAUMSTOFF-FORMGEGENSTÄNDEN UND SCHAUMSTOFF-FORMGEGENSTÄNDE

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Description

TECHNICAL FIELD

[0001] The present invention relates to method for producing molded foam articles, and molded foam articles.

[0002] Priority is claimed on Japanese Patent Application No. 2018-064240, filed March 29, 2018 and Japanese Patent Application No. 2018-098222, filed May 22, 2018.

BACKGROUND ART

[0003] In recent years, in the field of transportation equipment including automobiles and aircraft, weight reduction of members is being pursued for the purpose of improving fuel consumption. In order to lighten molded articles, the replacement of metals with resins and the application of resin molded foam articles are being investigated.

[0004] Among resins, liquid crystal polyesters are known as superior materials having heat resistance as well as superior mechanical properties and fluidity. Hereinafter, liquid crystal polyesters are sometimes referred to as "LCP". In order to reduce the weight of molded articles, while taking advantage of these characteristics of LCPs, foam molding of resin compositions containing an LCP are being investigated. Hereinafter, a resin composition containing an LCP is referred to as a "liquid crystal polyester resin composition".

[0005] In order to address these types of problems, supercritical fluids that function as physical foaming agents are being used favorably as foaming materials in the foam molding of liquid crystal polyester resin compositions.

[0006] For example, Patent Document 1 discloses a method for producing a molded foam article of a liquid crystal polyester resin composition that uses a supercritical fluid as a foaming material, a liquid crystal polyester resin composition, and a molded foam article produced from the composition.

[0007] Further, Patent Document 2 discloses a molded foam article of a liquid crystal polyester resin composition that uses a supercritical fluid as a foaming material. In Patent Document 2, the results of measuring and averaging the foam diameter of 500 random foam bubbles inside the molded article are also disclosed Further, Patent Document 3 discloses a molded foam article made from a resin composition and a supercritical fluid which is non-reactive with the liquid crystal polyester contained in the resin composition in a supercritical state. Further, Patent Document 4 relates to an expanded polyamide resin molding being reduced in weight and high load resistance without impairing the heat resistance of a polyamide resin.

[0008] The molded foam articles that use these liquid crystal polyester resin compositions feature excellent thermal insulation properties and superior levels of sink marks and warping, in addition to the inherent mechanical characteristics of the liquid crystal polyester.

[0009] Non-Patent Document 1 describes the relationship between the density and the number of bubble nuclei in a melted resin of a gas component (hereinafter referred to as the raw material gas) that is dissolved in the melted resin as a foaming material. The document suggests that as the amount of the raw material gas dissolved in the melted resin is increased, thereby increasing the density of the raw material gas in the melted resin, the number of bubble nuclei also increases. In other words, it can be reasoned by analogy that by increasing the bubble nuclei, foaming can be accelerated, and a molded article having a large number of bubbles can be produced. Based on these findings, it is hypothesized that by increasing the amount of a supercritical fluid introduced into a melted resin, a molded article having a large number of bubbles can be produced.

CITATION LIST

PATENT DOCUMENTS

[0010]

Patent Document 1: JP 602524-B
Patent Document 2: JP 2003-138054-A Patent Document 3: JP 2013 18504,
Patent Document 4: EP 2 636 703 A1

NON-PATENT DOCUMENT

[0011] Non-Patent Document 1: J. Colton and N.P. Suh, Polymer Engineering & Science, 27, 485 (1987)

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] However, the invention disclosed in Patent Document 1 has a problem in that some liquid crystal polyesters cannot be subjected to foam molding.

[0013] Further, in Patent Document 2, although the foam diameter is used as an indicator of the foamed state, the foamed state of the entire molded foam article is unclear. Generally, the foamed state of a molded foam article tends to deteriorate markedly near the flow terminal of a resin. Consequently, bubbles often coalesce to form non-uniform and huge cavities, and therefore a problem arises in that a simple evaluation of the foam diameter in a localized region in the molded article is unable to ascertain whether or not the foamed state of the entire molded foam article is uniform.

[0014] Moreover, when foam molding is conducted continuously, other problems sometimes arise, including instability in the weight of the molded foam articles with large fluctuations in the weight, and a lack of uniformity in the foamed state inside the molded articles.

[0015] The present invention has been developed in light of these circumstances, and has the objects of providing a method for producing molded foam articles that enables a resin composition containing an LCP to be foamed uniformly, and enables suppression of fluctuations in the weight of the molded foam articles, as well as providing a molded foam article.

MEANS TO SOLVE THE PROBLEMS

[0016] The inventors of the present invention discovered that by increasing the amount of supercritical fluid introduced when continuously molding LCP molded foam articles, not only did the foamed state of the produced molded articles lose uniformity, but fluctuation in the weight of the molded articles also increased.

[0017] Moreover, they also discovered that, when introducing a supercritical fluid into a melted resin, if the amount of supercritical fluid introduced was outside a specific range, then the foamed state of the produced molded foam articles lost uniformity. Further, the inventors also discovered that when the melt tension of the liquid crystal polyester was outside a specific range, not only did the foamed state of the produced molded articles lose uniformity, but fluctuation in the weight of the molded articles also increased.

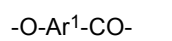
[0018] Based on the above findings, the inventors of the present invention discovered that by continuously repeating an operation for molding molded foam articles in which a specific amount of a supercritical fluid is introduced into and melt-kneaded with a resin composition containing a liquid crystal polyester having a melt tension within a specific range, a uniform foamed state could be achieved inside the molded articles.

[0019] That is, the present invention provides the following [1] to [9].

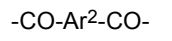
[1] A method for producing molded foam articles that molds molded foam articles continuously, the method comprising a step 1 of melting a resin composition including a liquid crystal polyester wherein the amount of the liquid crystal polyester, relative to the total mass of the resin composition, is greater than 30% by mass but not more than 100% by mass, a step 2 of using an introduction device to introduce at least 0.1 parts by mass but not more than 0.3 parts by mass, per 100 parts by mass of the liquid crystal polyester, of a foaming material formed from a supercritical fluid that is unreactive, in a supercritical state, with the liquid crystal polyester, and is a gas at normal temperature and normal pressure, and then melt-kneading the resultant mixture, a step 3 of injecting the melt-kneaded resin composition into a mold, and a step 4 of conducting foaming by lowering at least one of the pressure and the temperature of the foaming material to a value below the critical point of the foaming material, wherein step 1, step 2, step 3 and step 4 are repeated continuously in this order, and the method further comprises measuring an amount introduced of the supercritical fluid, and performing feedback control of the amount introduced of the supercritical fluid based on a measurement result; and the liquid crystal polyester has a melt tension at a temperature 20°C higher than the flow start temperature of at least 5 mN but not more than 100 mN.

[2] The method for producing molded foam articles according to [1], wherein the liquid crystal polyester has repeating units represented by general formulas (1), (2) and (3) shown below.

(1)



(2)



(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and one or more hydrogen atoms in Ar^1, Ar^2 and Ar^3 may each be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[3] The method for producing molded foam articles according to [1] or [2], wherein following injection of the melt-kneaded resin composition into the mold, the resin composition is foamed using the core-back method.

[4] The method for producing molded foam articles according to any one of [1] to [3], wherein the supercritical fluid is nitrogen.

[5] The method for producing molded foam articles according to any one of [1] to [4], wherein the resin composition comprises an inorganic filler in an amount exceeding 0 parts by mass but not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester.

[6] The method for producing molded foam articles according to any one of [1] to [5], wherein the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature is at least 200 Pa s but not more than 5,000 Pa s.

[7] A molded foam article that uses a resin composition comprising a liquid crystal polyester having repeating units represented by formulas (1), (2) and (3) shown below and also comprising an inorganic filler in an amount exceeding 0 parts by mass but not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester, and having a viscosity at a temperature 20°C higher than the flow start temperature of at least 200 Pa·s but not more than 5,000 Pa·s and a melt tension at a temperature 20°C higher than the flow start temperature of at least 5 mN but not more than 100 mN.

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and one or more hydrogen atoms in Ar^1, Ar^2 and Ar^3 may each be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[8] The molded foam article according to [7], having a thin-wall portion with a thickness of 4.0 mm or less.

[0020] In other words, the present invention includes the following aspects.

[1'] A method for producing molded foam articles that molds molded foam articles continuously, the method comprising continuously repeating the following step 1, step 2, step 3 and step 4 in this order, wherein

step 1 comprises melting a resin composition that includes a liquid crystal polyester, wherein the amount of liquid crystal polyester, relative to the total mass of the resin composition, is greater than 30% by mass but no more than 100% by mass,
step 2 comprises introducing, with an introduction device, a supercritical fluid that is unreactive, in a supercritical state, with the liquid crystal polyester, and is a gas at normal temperature and normal pressure, into the resin composition in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, and then melt-kneading the resultant mixture;
step 3 comprises injecting the melt-kneaded resin composition containing the supercritical fluid into a mold;
step 4 comprises conducting foaming by lowering at least one of the pressure and the temperature of the supercritical fluid contained in the resin composition to a value below the critical point of the supercritical fluid,
the method further comprises measuring an amount introduced of the supercritical fluid, and performing feedback control of the amount introduced of the supercritical fluid based on a measurement result; and
thereby producing a molded foam body: and
the liquid crystal polyester has a melt tension at a temperature 20°C higher than the flow start temperature of at least 5 mN but not more than 100 mN.

[2'] The method for producing molded foam articles according to [1'], wherein the liquid crystal polyester has a repeating unit represented by general formula (1) shown below, a repeating unit represented by general formula (2) shown below, and a repeating unit represented by general formula (3) shown below.

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[3'] The method for producing molded foam articles according to [1'] or [2'], wherein following injection of the melt-kneaded resin composition containing the supercritical fluid into the mold, the resin composition containing the supercritical fluid is foamed using the core-back method.
[4'] The method for producing molded foam articles according to any one of [1'] to [3'], wherein the supercritical fluid is nitrogen.
[5'] The method for producing molded foam articles according to any one of [1'] to [4'], wherein the resin composition comprises an inorganic filler in an amount exceeding 0 parts by mass but not more than 100 parts by mass per 100

parts by mass of the liquid crystal polyester.

[6'] The method for producing molded foam articles according to any one of [1'] to [5'], wherein the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature is at least 200 Pa·s but not more than 5,000 Pa·s.

[7'] A molded foam article that is foam molded from a foaming material and a resin composition, wherein

the resin composition comprises a liquid crystal polyester having a repeating unit represented by general formula (1) shown below, a repeating unit represented by general formula (2) shown below and a repeating unit represented by general formula (3) shown below, and also comprises an inorganic filler,
the amount of the inorganic filler exceeds 0 parts by mass but is not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester,
the resin composition has a viscosity at a temperature 20°C higher than the flow start temperature of the resin composition of at least 200 Pa·s but not more than 5,000 Pa·s, and
the liquid crystal polyester has a melt tension at a temperature 20°C higher than the flow start temperature of the liquid crystal polyester of at least 5 mN but not more than 100 mN.

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[8'] The molded foam article according to [7'], having a thin-wall portion with a thickness of 4.0 mm or less.

EFFECTS OF THE INVENTION

[0021] The present invention can provide a method for producing molded foam articles that enables a resin composition containing an LCP to be foamed uniformly, and enables suppression of fluctuations in the weight of the molded foam articles, and can also provide a molded foam article.

BRIEF DESCRIPTION OF DRAWINGS

[0022] FIG. 1 is a schematic illustration of an injection molding machine used in the production of molded foam articles of an embodiment of the present invention.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

<Method for Producing Molded Foam Articles>

[0023] One embodiment of the present invention is a method for producing molded foam articles that molds molded

foam articles continuously, according to claim 1.

[0024] The method for producing molded foam articles of this embodiment comprises a step 1 of melting a resin composition including a liquid crystal polyester, a step 2 of introducing, with an introduction device, a supercritical fluid that is unreactive, in a supercritical state, with the liquid crystal polyester, and is a gas at normal temperature and normal pressure, into the resin composition in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, and then melt-kneading the resultant mixture, a step 3 of injecting the melt-kneaded resin composition containing the supercritical fluid into a mold, and a step 4 of conducting foaming by lowering at least one of the pressure and the temperature of the supercritical fluid contained in the resin composition to a value below the critical point of the supercritical fluid, thereby producing a molded foam article. Moreover, step 1, step 2, step 3 and step 4 are repeated continuously in this order.

[0025] Here, "continuously" means that the series of molding operations from step 1 to step 4 is repeated at least twice. In an embodiment of the present invention, the series of molding operations is preferably repeated at least 10 times, more preferably repeated at least 20 times, and particularly preferably repeated 30 or more times.

[0026] When the number of repetitions of the above molding operations exceeds 10, the dispersed state of the supercritical fluid contained in the melted resin (the resin composition containing the melted liquid crystal polyester) inside a cylinder 111 becomes uniform, and molded foam articles having a uniform foamed state can be produced.

[0027] Here, "uniform" means a state in which the melted resin and the supercritical fluid have formed a single phase.

[0028] On the other hand, those cases where the introduction of the supercritical fluid is not performed after every repetition of step 1, but is rather performed intermittently, are deemed to be excluded from the meaning of "continuous". In other words, within the series of molding operations from step 1 to step 4, cases where step 2 is omitted once every two repetitions, or omitted twice every three repetitions or the like, are deemed to be excluded from the meaning of "continuous".

[0029] FIG. 1 is a schematic illustration of an injection molding machine used for producing molded foam bodies according to an embodiment of the present invention.

[0030] This injection molding machine 1 is a machine for producing molded foam bodies of a prescribed shape using the resin composition and the supercritical fluid described below described below, and has a main body 11, a mold 12, and a supercritical fluid introduction device 21 for introducing the supercritical fluid into the main body 11.

[0031] The introduction device 21 comprises a gas cylinder 211 filled with a raw material gas of the supercritical fluid mentioned above, a pressurizer 212 for increasing the pressure of the raw material gas from the gas cylinder 211 to critical pressure, and a control valve 213 for controlling the amount of the raw material gas that has been pressurized to critical pressure (the supercritical fluid) that is introduced into the cylinder 111. The temperature of the raw material gas increases due to adiabatic compression of the raw material gas in the pressurizer 212, but in those cases where the temperature reached as a result of this temperature increase does not satisfy the critical temperature, if necessary, a heater may be used to increase the temperature of the raw material gas from the gas cylinder 211 to the critical temperature.

[0032] Next is a description of a method for producing molded foam bodies using this injection molding machine 1.

[Step 1]

[0033] Step 1 is a step that includes melting the resin composition containing a liquid crystal polyester.

[0034] First, the resin composition described above is fed into the cylinder 111 from a hopper 113, and the resin composition is melted (plasticized) by conducting heated melt-kneading inside the cylinder 111. In embodiments of the present invention, "plasticization metering" means the operation of melting (plasticizing) pellets of the resin composition in a short period of time by screw rotation, and loading the inside of the cylinder 111 with an amount of the resin composition required to fill the next injection process.

[Step 2]

[0035] Step 2 is a step that includes using a supercritical fluid that is unreactive, in a supercritical state, with the liquid crystal polyester, and is a gas at normal temperature and normal pressure (25°C, 1,013 hPa) as a foaming material, and using the introduction device to introduce the foaming material into the melted resin composition in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester and then melt-knead the resultant mixture.

[0036] In step 2, first, the gas cylinder 211 is opened, and the raw material gas is converted to a supercritical fluid by increasing the pressure and the temperature to values at least as high as the critical point in the pressurizer 212. By opening the control valve 213, the obtained supercritical fluid is introduced into the cylinder 111 and impregnated into the melted resin composition. An amount of the supercritical fluid of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester is introduced into the melted resin composition by

the introduction device 21 and melt-kneaded during each plasticization metering.

[0037] The introduction device 21 comprises a feedback unit that measures the amount introduced of the supercritical fluid and can perform feedback control based on the measurement result (an example of the supercritical fluid introduction device is the T-100J manufactured by Trexel, Inc.). By using feedback control, oversupply or undersupply of the supercritical fluid can be suppressed. Specifically, the amount introduced of the supercritical fluid is controlled by monitoring and controlling the introduction time period and the differential pressure and the like of the supercritical fluid. This enables the abovementioned specific amount of the supercritical fluid to be introduced during each plasticization metering.

[0038] By ensuring that the amount introduced of the supercritical fluid is at least 0.1 parts by mass per 100 parts by mass of the liquid crystal polyester, the foaming of the resin proceeds adequately. Further, by ensuring that the amount is not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, the foamed state inside the molded articles becomes uniform. If the amount introduced of the supercritical fluid exceeds 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, then the foamed state inside the molded articles can sometimes lose uniformity.

[0039] Further, if the amount introduced of the supercritical fluid is less than 0.1 parts by mass per 100 parts by mass of the liquid crystal polyester, then foaming of the resin may not proceed adequately, and molded foam articles may be unobtainable.

[0040] Moreover, by introducing the above prescribed amount of the supercritical fluid during each repetition of plasticization metering, fluctuations in the mass between individual molded articles (the standard deviation of the molded article weight) can be suppressed. In contrast, in those cases where the above prescribed amount of the supercritical fluid is not introduced during each plasticization metering, the foamed state inside the molded articles can sometimes lose uniformity. For example, even if the amount introduced of the supercritical fluid is at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, if the above prescribed amount of the supercritical fluid is only introduced at a frequency of once for every three repetitions of plasticization metering, then the foamed state inside the molded articles may sometimes lose uniformity.

[Step 3]

[0041] Step 3 is a step that includes injecting the melt-kneaded resin composition containing the supercritical fluid into a mold.

[0042] Using the screw 112, the melt-kneaded melted resin containing the supercritical fluid (the melted resin composition) inside the cylinder 111 is moved and injected into the mold 12. At this time, in order to maintain a state in which the melted resin is impregnated with the supercritical fluid, the mold 12 may be clamped or subjected to a counter pressure until the injection of the melted resin containing the supercritical fluid into the mold 12 is complete.

[Step 4]

[0043] Step 4 is a step that includes conducting foaming by lowering at least one of the pressure and the temperature of the supercritical fluid contained in the melt-kneaded resin composition to a value below the critical point of the supercritical fluid.

[0044] In an embodiment of the present invention, the injection molding method using the mold 12 may be any one of the short shot method, the full shot method and the core-back method. From the viewpoint of enabling proactive foaming by expanding the mold volume following filling of the mold with the melted resin, the core-back method is preferred.

[0045] The core-back method is a method in which, for example, by using a mold for which the cavity volume can be changed, the cavity volume is expanded after the mold has been filled with the melted resin, and includes both a method that utilizes the action of a mold sliding core, and a method that relies on the action of a movable platen of the molding machine.

[0046] The melted resin containing the supercritical fluid inside the cylinder 111 undergoes a fall in temperature during the step of using the screw 112 to inject the melted resin from inside the cylinder 1 1 1 into the mold 12 which has been adjusted to a desired temperature with a heater or the like. Moreover, the pressure, which was at least as high as the critical pressure, approaches normal pressure, and the solubility of the supercritical fluid contained in the melted resin deteriorates, causing a transition to the gaseous state. The supercritical fluid contained in the melted resin changes to a gaseous form, the volume expands, and a molded foam body is obtained. Subsequently, following cooling and solidification of the resin inside the mold 12, the molded article is removed from the mold 12 after a prescribed cooling time. By using the operations described above, molded foam articles can be obtained by injection molding.

[0047] In embodiments of the present invention, the steps 1 to 4 are repeated in this order. By executing step 2 and introducing a specific amount of the supercritical fluid each repetition, the foaming of the resin can be made more uniform.

[0048] As a result, fluctuations in the weight of the molded articles can be suppressed.

[0049] In this description, "weight fluctuations in the molded articles" means fluctuations between individual products.

(Supercritical Fluid)

[0050] The foaming material according to embodiments of the present invention is a supercritical fluid which, in the supercritical state, is unreactive with the liquid crystal polyester, and which is a gas at normal temperature and normal pressure.

[0051] Here, "supercritical fluid" is a term that indicates the state of a substance, which is not gaseous, liquid nor solid, exhibited under conditions equal to or exceeding a specific temperature and pressure (critical point). The critical point that represents a specific temperature and pressure are determined by the type of substance. A supercritical fluid exhibits superior permeability (solubility) in the melted resin compared with the substance in the gaseous state or liquid state, and can be dispersed uniformly within the melted resin.

[0052] In embodiments of the present invention, for example, inert gases such as carbon dioxide, nitrogen and helium, and air and the like are preferable as the supercritical fluid. In embodiments of the present invention, carbon dioxide and nitrogen are more preferable. Moreover, the critical point for nitrogen occurs at a temperature of -147°C and a pressure of 3.4 MPa, and therefore normal temperature (25°C) is higher than the critical temperature. Accordingly, the supercritical fluid can be adjusted by only controlling the pressure, meaning handling is easier, and therefore nitrogen is particularly desirable.

<<Resin Composition Containing Liquid Crystal Polyester>>

[0053] The resin composition containing a liquid crystal polyester according to an embodiment of the present invention contains a liquid crystal polyester and an arbitrary inorganic filler.

(Liquid Crystal Polyester)

[0054] The liquid crystal polyester according to the present invention has a melt tension at a temperature 20°C higher than the flow start temperature of at least 5 mN but not more than 100 mN.

[0055] Here, the flow start temperature is also called the flow temperature or fluidity temperature, and acts as an indicator of the molding temperature during injection molding of the liquid crystal polyester. During injection molding, the molding is generally conducted at a temperature higher than the flow start temperature. The flow start temperature is measured using a capillary rheometer having a nozzle with an internal diameter of 1 mm and a length of 10 mm, and represents the temperature at which the melt viscosity reaches 4,800 Pa·s (48,000 poise) when the heated and melted liquid crystal polyester is extruded from the nozzle while the temperature is raised at a rate of 4°C/minute under a loading of 9.8 MPa (100 kg/cm^2).

[0056] The melt tension can be measured using the following method.

[0057] Using a capillary rheometer, the liquid crystal polyester is extruded from a nozzle having an internal diameter of 1 mm and a length of 10 mm, at a temperature 20°C higher than the flow start temperature of the liquid crystal polyester contained in the resin composition, by lowering a piston (?0 mm) at a rate of 10 mm/minute. The melt tension at this time is measured.

[0058] In the present invention, the melt tension of the liquid crystal polyester is at least 5 mN, and is preferably at least 10 mN, and more preferably 20 mN or greater.

[0059] Further, the melt tension is preferably not more than 90 mN, more preferably not more than 80 mN, and particularly preferably 75 mN or less. If the melt tension of the liquid crystal polyester is less than 5 mN, then when the resin composition (melted resin) containing the supercritical fluid is foamed by reducing the pressure inside the mold, the gas bubbles are more likely to coalesce, meaning molded foam articles having a non-uniform foamed state are sometimes obtained. On the other hand, if the melt tension of the liquid crystal polyester exceeds 100 mN, then the injection pressure during injection molding may sometimes increase excessively, making molding impossible.

[0060] The above upper limit and lower limit values may be combined as desired.

[0061] In one aspect, the melt tension of the liquid crystal polyester according to the present invention is preferably at least 5 mN but not more than 90 mN, more preferably at least 10 mN but not more than 80 mN, and particularly preferably at least 20 mN but not more than 75 mN.

[0062] In another aspect, the melt tension of the liquid crystal polyester according to the present invention may be at least 5 mN but not more than 71 mN, or at least 14 mN but not more than 71 mN.

[0063] Provided the melt tension falls within the above range, the foamed state inside the molded articles becomes more uniform. The melt tension may be adjusted by increasing the molecular weight of the liquid crystal polyester, or may be controlled by adjusting the amount of inorganic filler or the like that is added.

[0064] If a liquid crystal polyester having a melt tension within the above range is used, then when the supercritical fluid contained in the melted resin is subjected to a reduction in pressure and foaming inside the mold, coalescence of the gas bubbles is less likely to occur, and the bubbles can be more easily uniformly micronized, enabling molded foam

articles having a uniform foamed state to be produced.

[0065] The liquid crystal polyester according to an embodiment of the present invention has repeating units represented by general formulas (1), (2) and (3) shown below.

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[0066] In the above general formulas (1) to (3), examples of the halogen atom that may substitute at least one hydrogen atom in the group represented by Ar^1, Ar^2 or Ar^3 include a fluorine atom, chlorine atom, bromine atom and iodine atom.

[0067] In the above general formulas (1) to (3), the alkyl group that may substitute at least one hydrogen atom in the group represented by Ar^1, Ar^2 or Ar^3 is preferably an alkyl group of 1 to 10 carbon atoms, and examples include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, sec-butyl group, tert-butyl group, n-hexyl group, n-heptyl group, 2-ethylhexyl group, n-octyl group, n-nonyl group and n-decyl group.

[0068] In the above general formulas (1) to (3), the aryl group that may substitute at least one hydrogen atom in the group represented by Ar^1, Ar^2 or Ar^3 is preferably an aryl group of 6 to 20 carbon atoms, and examples include monocyclic aromatic groups such as a phenyl group, o-tolyl group, m-tolyl group and p-tolyl group, and condensed ring aromatic groups such as a 1-naphthyl group and 2-naphthyl group.

[0069] In the above general formulas (1) to (3), in those cases where at least one hydrogen atom in the group represented by Ar^1, Ar^2 or Ar^3 is substituted with one of these groups, the number of substituents in each group represented by Ar^1, Ar^2 or Ar^3 is, independently, preferably either 1 or 2, and is more preferably 1.

[0070] In the above general formula (4), the alkylidene group is preferably an alkylidene group of 1 to 10 carbon atoms, and examples include a methylene group, ethylidene group, isopropylidene group, n-butylidene group and 2-ethylhexylidene group.

[0071] The repeating unit represented by general formula (1) is preferably a repeating unit in which Ar^1 is a 1,4-phenylene group (for example, a repeating unit derived from p-hydroxybenzoic acid), a repeating unit in which Ar^1 is a 2,6-naphthylene group (for example, a repeating unit derived from 6-hydroxy-2-naphthoic acid), or a repeating unit in which Ar^1 is a 4,4'-biphenylylene group.

[0072] Examples of the monomer that forms the repeating unit represented by general formula (1) include 6-hydroxy-2-naphthoic acid, p-hydroxybenzoic acid and 4-(4-hydroxyphenyl)benzoic acid, as well as monomers in which a hydrogen atom on the benzene ring or naphthalene ring of one of these compounds has been substituted with a halogen atom, an alkyl group of 1 to 10 carbon atoms or an aryl group. Moreover, the monomer may also be used in the form of an ester-forming derivative described below.

[0073] The repeating unit represented by general formula (2) is preferably a repeating unit in which Ar^2 is a 1,4-phenylene group (for example, a repeating unit derived from terephthalic acid), a repeating unit in which Ar^2 is a 1,3-phenylene group (for example, a repeating unit derived from isophthalic acid), a repeating unit in which Ar^2 is a 2,6-naphthylene group (for example, a repeating unit derived from 2,6-naphthalenedicarboxylic acid), or a repeating unit in which Ar^2 is a diphenyl ether-4,4'-diyl group (for example, a repeating unit derived from diphenyl ether-4,4'-dicarboxylic

acid), and is more preferably a repeating unit in which Ar^2 is a 1,4-phenylene group, a repeating unit in which Ar^2 is a 1,3-phenylene group, or a repeating unit in which Ar^2 is a 2,6-naphthylene group.

[0074] Examples of the monomer that forms the repeating unit represented by general formula (2) include 2,6-naphthalenedicarboxylic acid, terephthalic acid, isophthalic acid, and biphenyl-4,4'-dicarboxylic acid, as well as monomers in which a hydrogen atom on the benzene ring or naphthalene ring of one of these compounds has been substituted with a halogen atom, an alkyl group of 1 to 10 carbon atoms or an aryl group. Moreover, the monomer may also be used in the form of an ester-forming derivative described below.

[0075] The repeating unit represented by general formula (3) is preferably a repeating unit in which Ar^3 is a 1,4-phenylene group (for example, a repeating unit derived from hydroquinone, a repeating unit derived from p-aminophenol, or a repeating unit derived from p-phenylenediamine), or a repeating unit in which Ar^3 is a 4,4'-biphnylylene group (for example, a repeating unit derived from 4,4'-dihydroxybiphenyl, a repeating unit derived from 4-amino-4'-hydroxybiphenyl, or a repeating unit derived from 4,4'-diaminobiphenyl).

[0076] Examples of the monomer that forms the repeating unit represented by general formula (3) include 2,6-naphthol, hydroquinone, resorcin and 4,4'-dihydroxybiphenyl, as well as monomers in which a hydrogen atom on the benzene ring or naphthalene ring of one of these compounds has been substituted with a halogen atom, an alkyl group of 1 to 10 carbon atoms or an aryl group. Moreover, the monomer may also be used in the form of an ester-forming derivative described below.

[0077] In order to facilitate the polymerization in the process for producing the polyester, an ester-forming derivative is preferably used as the monomer for forming the repeating unit represented by formula (1), the repeating unit represented by formula (2) or the repeating unit represented by formula (3). This ester-forming derivative describes a monomer having the type of group that promotes an ester-producing reaction, and specific examples include highly reactive derivatives, including ester-forming derivatives in which the carboxylic acid group in a monomer molecule has been converted to an acid halide or an acid anhydride, and ester-forming derivatives in which the hydroxyl group in a monomer molecule has been converted to a lower carboxylate ester group.

[0078] The amount of the repeating unit (1) in the liquid crystal polyester, when the total amount of the repeating unit (1), the repeating unit (2) and the repeating unit (3) is deemed 100 mol%, is preferably at least 30 mol%, more preferably at least 30 mol% but not more than 80 mol%, even more preferably at least 40 mol% but not more than 70 mol%, and still more preferably at least 45 mol% but not more than 65 mol%.

[0079] The amount of the repeating unit (2) in the liquid crystal polyester, when the total amount of the repeating unit (1), the repeating unit (2) and the repeating unit (3) is deemed 100 mol%, is preferably not more than 35 mol%, more preferably at least 10 mol% but not more than 35 mol%, even more preferably at least 15 mol% but not more than 30 mol%, and still more preferably at least 17.5 mol% but not more than 27.5 mol%.

[0080] The amount of the repeating unit (3) in the liquid crystal polyester, when the total amount of the repeating unit (1), the repeating unit (2) and the repeating unit (3) is deemed 100 mol%, is preferably not more than 35 mol%, more preferably at least 10 mol% but not more than 35 mol%, even more preferably at least 15 mol% but not more than 30 mol%, and still more preferably at least 17.5 mol% but not more than 27.5 mol%.

[0081] In other words, when the total amount of the repeating unit (1), the repeating unit (2) and the repeating unit (3) in the liquid crystal polyester is deemed 100 mol%, it is preferable that the amount of the repeating unit (1) is at least 30 mol% but not more than 80 mol%, the amount of the repeating unit (2) is at least 10 mol% but not more than 35 mol%, and the amount of the repeating unit (3) is at least 10 mol% but not more than 35 mol%.

[0082] Provided the liquid crystal polyester includes an amount of the repeating unit (1) that falls within the above range, the melt fluidity, the heat resistance, and the strength and rigidity can be more easily improved.

[0083] The liquid crystal polyester may have only one type of each of the repeating units (1) to (3), or may have two or more types of one or more of the repeating units. Further, the liquid crystal polyester may also have one, or two or more, other repeating units besides the repeating units (1) to (3), but the amount of these other repeating units, when the total amount of all the repeating units is deemed to be 100 mol%, is preferably at least 0 mol% but not more than 10 mol%, and more preferably at least 0 mol% but not more than 5 mol%.

[0084] In terms of facilitating a lowering of the melt viscosity, the liquid crystal polyester preferably has, as the repeating unit (3), a repeating unit in which X and Y are both oxygen atoms, namely a repeating unit derived from a prescribed aromatic diol, and it is more preferable that the liquid crystal polyester has only repeating units in which X and Y are both oxygen atoms as the repeating unit (3).

[0085] The liquid crystal polyester is preferably produced by conducting a melt polymerization of the raw material monomers corresponding with the repeating units that constitute the liquid crystal polyester, and subjecting the thus obtained polymer (prepolymer) to a solid phase polymerization. This enables a high-molecular weight liquid crystal polyester having superior heat resistance, strength and rigidity to be produced with good operability. The melt polymerization may be performed in the presence of a catalyst, and examples of the catalyst include metal compounds such as magnesium acetate, stannous acetate, tetrabutyl titanate, lead acetate, sodium acetate, potassium acetate and antimony trioxide, and nitrogen-containing heterocyclic compounds such as N,N-dimethylaminopyridine and 1-methylimidazole,

with a nitrogen-containing heterocyclic compound being preferable.

[0086] The flow start temperature of the liquid crystal polyester is preferably at least 270°C, more preferably at least 270°C but not more than 400°C, and even more preferably at least 280°C but not more than 380°C. The higher the flow start temperature of the liquid crystal polyester, the more easily the heat resistance and the strength, rigidity and impact resistance can be improved, but if the flow start temperature is too high, then a high temperature is required to melt the polyester, thermal degradation during molding becomes more likely, and the viscosity upon melting tends to increase, causing a deterioration in fluidity. In one aspect, provided the flow start temperature of the liquid crystal polyester falls within the above range, the heat resistance, and the strength, rigidity and impact resistance of the obtained molded articles can be improved, thermal degradation during molding becomes less likely, and a suitable viscosity and fluidity are achieved upon melting.

[0087] A single type of liquid crystal polyester may be used alone, or a combination of two or more types may be used.

[0088] In one aspect, the amount of the liquid crystal polyester according to the present invention, relative to the total mass of the resin composition, is greater than 30% by mass but not more than 100% by mass, more preferably at least 40% by mass but not more than 90% by mass, and particularly preferably at least 50% by mass but not more than 80% by mass.

(Inorganic Filler)

[0089] Examples of inorganic fillers include ceramic fibers such as glass fiber, silica fiber and alumina fiber, silica-alumina fiber, metal fibers such as stainless steel fiber, as well as talc, mica, flake graphite, wollastonite, barium sulfate and calcium carbonate. Examples of the glass fiber include fibers produced by various methods, such as chopped glass fiber and milled glass fiber. The mica may be muscovite, phlogopite, fluorphlogopite or tetrasilicic mica. The flake graphite may be natural flake graphite or synthetic flake graphite.

[0090] In an embodiment of the present invention, the inorganic filler is preferably glass fiber.

[0091] The number average fiber length of the glass fiber following melt-kneading is preferably at least 50 μm but not more than 500 μm. Further, the number average fiber diameter of the glass fiber following melt-kneading is preferably at least 6 μm but not more than 18 μm.

[0092] In this description, the number average fiber length and the number average fiber diameter of the glass fiber following melt-kneading can be measured by electron microscope observation.

[0093] A single type of glass fiber may be used alone, or a combination of two or more types may be used.

[0094] In an embodiment of the present invention, the blend amount of the inorganic filler, per 100 parts by mass of the liquid crystal polyester, is preferably greater than 0 parts by mass but not more than 100 parts by mass, more preferably at least 10 parts by mass but not more than 90 parts by mass, and particularly preferably at least 20 parts by mass but not more than 80 parts by mass.

(Other Components)

[0095] The resin composition according to an embodiment of the present invention may also contain other components that do not correspond with either the liquid crystal polyester or the inorganic filler, provided these other components do not impair the effects of the present invention.

[0096] Examples of these other components include fillers other than the inorganic filler (hereinafter sometimes referred to as "other fillers"), additives, and resins besides the liquid crystal polyester (hereinafter sometimes referred to as "other resins").

[0097] A single type of these other components may be used alone, or a combination of two or more types may be used.

[0098] In those cases where the resin composition according to an embodiment of the present invention contains another filler, the amount of the other filler is preferably greater than 0 parts by mass but not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester.

[0099] Examples of the additives include antioxidants, heat stabilizers, ultraviolet absorbers, antistatic agents, surfactants, flame retardants and colorants.

[0100] In those cases where the resin composition according to an embodiment of the present invention contains an additive, the amount of the additive is preferably greater than 0 parts by mass but not more than 5 parts by mass per 100 parts by mass of the total mass of the liquid crystal polyester and the inorganic filler.

[0101] Examples of the other resins include thermoplastic resins such as polyethersulfones, polyetherimides, polysulfones, polyarylates, polyamides, polyesters, polyphenylene sulfides, polyetherketones and modified polyphenylene ethers, and combinations of two or more types of these resins may also be used.

[0102] In those cases where the resin composition according to an embodiment of the present invention contains another resin, the amount of the other resin is preferably greater than 0 parts by mass but not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester.

[0103] The resin composition according to an embodiment of the present invention preferably has a viscosity at a temperature 20°C higher than the flow start temperature that is at least 200 Pa·s but not more than 5,000 Pa·s. Provided the viscosity of the resin composition falls within the above range, the foamed state inside the molded articles becomes more uniform. If the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature is less than 200 Pa·s, then when the melted resin obtained by melt-kneading the resin composition containing the supercritical fluid is subjected to a reduction in pressure and foaming inside the mold, coalescence of the gas bubbles is more likely to occur, and molded foam articles having a non-uniform foamed state can sometimes occur. On the other hand, if the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature exceeds 5,000 Pa·s, then the viscosity of the resin composition is overly high, which can sometimes make foaming impossible, meaning molded foam articles cannot be obtained.

[0104] In one aspect, the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature may be at least 230 Pa·s but not more than 4,000 Pa·s, or at least 1,600 Pa·s but not more than 4,000 Pa·s.

[0105] The resin composition can be produced by mixing the liquid crystal polyester, the inorganic filler and any other desired components, either in a single batch or in an appropriate order.

[0106] The resin composition is preferably pelletized by using an extruder to perform melt-kneading of the liquid crystal polyester, the inorganic filler, and any other desired components.

[0107] The extruder is preferably a device having a cylinder, one or more screws disposed inside the cylinder, and one or more supply ports provided on the cylinder, and is more preferably a device that also has one or more vents provided in the cylinder.

<Molded Foam Article Molded from Resin Composition>

[0108] One embodiment of the present invention is a molded foam article, according to claim 7, that is foam molded from a foaming material and a resin composition, wherein the resin composition comprises a liquid crystal polyester having a repeating unit represented by general formula (1) shown below, a repeating unit represented by general formula (2) shown below and a repeating unit represented by general formula (3) shown below, and also comprises an inorganic filler, the amount of the inorganic filler exceeds 0 parts by mass but is not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester, the resin composition has a viscosity at a temperature 20°C higher than the flow start temperature of the resin composition of at least 200 Pa·s but not more than 5,000 Pa·s, and the liquid crystal polyester has a melt tension at a temperature 20°C higher than the flow start temperature of the liquid crystal polyester of at least 5 mN but not more than 100 mN.

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

(In the formulas, Ar^1 represents a phenylene group, naphthylene group or biphenylylene group; Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below; X and Y each independently represent an oxygen atom or an imino group; and at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group.)

(4)

$$-Ar^4-Z-Ar^5-$$

(In the formula, Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.)

[0109] The molded foam article of an embodiment of the present invention preferably has a thin-wall portion with a thickness of 4.0 mm or less.

[0110] The molded foam article of an embodiment of the present invention has a thickness that is preferably not more than 4.0 mm, more preferably not more than 3.5 mm, and particularly preferably 3.0 mm or less.

[0111] An example of the lower limit for the thickness is at least 0.1 mm, preferably at least 0.3 mm, and particularly preferably 0.5 m or greater. Provided the thickness is at least as large as the above lower limit, the molded article can be more easily foamed before cooling and solidification of the resin in the mold. As a result, the weight of the molded article can be adequately reduced.

[0112] The molded foam article of an embodiment of the present invention may be a molded foam article having a thin-wall portion with a thickness of 4.0 mm or less and a thick-wall portion with a thickness exceeding 4.0 mm, or may be a molded foam article in which the thickness of the maximum thickness portion is 4.0 mm or less.

[0113] In this description, the "thickness" of the molded foam article can be measured with a micrometer.

[0114] A "thin-wall portion" means a region in which the thickness of the molded foam article is at least 0.1 mm but not more than 4 mm.

[0115] A "thick-wall portion" means a region in which the thickness of the molded foam article is greater than 4 mm but not more than 30 mm.

[0116] The "maximum thickness portion" means the region in which the thickness of the molded foam article is greatest.

[0117] As a result of intensive investigation, the inventors of the present invention discovered that in molded foam articles of embodiments of the present invention, the strength was particularly superior when the thickness of the articles was reduced. To provide an example, when molded foam articles formed from liquid crystal polyesters having similar amounts of weight reduction are compared, the more the thickness of the molded foam article is reduced, the greater the improvement in the strength retention ratio of the average flexural strength of the molded foam article between before and after the thickness reduction. In solid molded articles formed from liquid crystal polyesters, it is known that because the molecular orientation of the skin layer is superior to the molecular orientation of the core layer, the strength layer of the skin layer itself has an effect on the strength of the overall solid molded article. On the other hand, in molded foam articles formed from liquid crystal polyesters, it is surmised that as the thickness of the molded article is reduced, the effect that the strength of the skin layer has on the strength of the overall molded foam article is even greater than that observed in solid molded articles.

[0118] Examples of components formed from molded foam articles of embodiments of the present invention include bobbins such as optical pickup bobbins and transformer bobbins; relay components such as relay cases, relay bases, relay sprues and relay armatures; connectors such as RIMM, DDR and CPU sockets, as well as S/O, DIMM and Board to Board connectors, FPC connectors and card connectors; reflectors such as lamp reflectors and LED reflectors; holders such as lamp holders and heater holders; diaphragms such as speaker diaphragms; separation claws such as separation claws for copiers and separation claws for printers; camera module components; switch components; motor components; sensor components; hard disk drive components; tableware such as ovenware; vehicle components (including instrument panels, door trims, roofs, aero parts, and other structural members); aircraft components; and sealing members such as sealing members for semiconductor elements and sealing members for coils.

[0119] In one aspect, a method for producing molded foam articles according to an embodiment of the present invention, which molds molded foam articles continuously, comprises:

repeating at least twice the following step 1, step 2, step 3 and step 4 in this order; wherein

step 1 comprises melting a resin composition that includes a liquid crystal polyester;

step 2 comprises introducing, with an introduction device, a supercritical fluid which, in a supercritical state and in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, is unreactive with the liquid crystal polyester and which is a gas at normal temperature and normal pressure, into the resin composition in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, and then melt-kneading the resultant mixture;

step 3 comprises injecting the melt-kneaded resin composition containing the supercritical fluid into a mold;

step 4 comprises conducting foaming by lowering at least one of the pressure and the temperature of the supercritical fluid contained in the resin composition to a value below the critical point of the supercritical fluid, thereby producing a molded foam article;

the liquid crystal polyester is a liquid crystal polyester composed of a repeating unit (1) in which the abovementioned Ar^1 is a 2,6-naphthylene group, a repeating unit (2) in which the abovementioned Ar^2 is a 2,6-naphthylene group, a repeating unit (2) in which the abovementioned Ar^2 is a 1,4-phenylene group, and a repeating unit (3) in which the abovementioned Ar^3 is a 1,4-phenylene group, or

a liquid crystal polyester composed of a repeating unit (1) in which the abovementioned Ar^1 is a 1,4-phenylene group, a repeating unit (2) in which the abovementioned Ar^2 is a 1,4-phenylene group, a repeating unit (2) in which the abovementioned Ar^2 is a 1,3-phenylene group, and a repeating unit (3) in which the abovementioned Ar^3 is a 4,4'-biphenylylene group, and

when the total amount of the repeating unit (1), the repeating unit (2) and the repeating unit (3) is deemed 100 mol%,

the amount of the repeating unit (1) is at least 30 mol% but not more than 80 mol%, the amount of the repeating unit (2) is at least 10 mol% but not more than 35 mol%, and the amount of the repeating unit (3) is at least 10 mol% but not more than 35 mol%;
the liquid crystal polyester has a melt tension at a temperature 20°C higher than the flow start temperature of at least 5 mN but not more than 100 mN (preferably at least 5 mN but not more than 71 mN, and more preferably at least 14 mN but not more than 71 mN); and
the viscosity of the resin composition at a temperature 20°C higher than the flow start temperature of the resin composition is at least 200 Pa·s but not more than 5,000 Pa s (preferably at least 230 Pa·s but not more than 4,000 Pa·s, and more preferably at least 1,600 Pa·s but not more than 4,000 Pa·s).

EXAMPLES

[0120] The present invention is described below in further detail using a series of examples, but the present invention is in no way limited by the following examples.

(Melt Tension of Neat LCP)

[0121] For the liquid crystal polyester contained in the resin composition, a capillary rheometer was used to extrude the liquid crystal polyester, at a temperature 20°C higher than the flow start temperature of the liquid crystal polyester contained in the composition, from a nozzle having an internal diameter of 1 mm and a length of 10 mm, by lowering a piston (?0 mm) at a rate of 10 mm/minute, and the melt tension was measured (units: mN).

(Melt Viscosity of Resin Composition)

[0122] Using a parallel plate rheometer, the resin composition was melted at a temperature 80°C higher than the flow start temperature of the resin composition, the melt viscosity of the resin composition was measured while the temperature was lowered at a rate of 5°C per minute using a temperature reduction method, and the melt viscosity at a temperature 20°C higher than the flow start temperature of the resin composition was measured (units: Pa·s).

(Voids)

[0123] Voids are deemed to be cavities having a size of at least 0.1 mm^3 inside a molded foam article.

(Void Ratio)

[0124] The void ratio is the ratio (volumetric fraction) of the total volume of the abovementioned voids inside the molded foam article relative to the volume of the molded foam article, and was determined using a molded foam article of 150 mm ?150 mm ?thickness 2.4 mm, by using a three-dimensional X-ray CT system (TOSCANER 32300μFD, manufactured by Toshiba Corporation) to measure the void ratio inside the molded article, and then calculating the void ratio using analysis software VG STUDIO MAX. Because the shape of the molded articles was the uniform shape described above, a smaller average weight for the obtained molded article indicates improved weight reduction by foaming.

(Foamed State Inside Molded Article)

[0125] The foamed state inside a molded article was evaluated against the following criteria.

A: when the void ratio is less than 0.5%
B: when the void ratio is at least 0.5% but less than 1.0%
C: when the void ratio is at least 1.0% but less than 1.5%
D: when the void ratio is 1.5% or greater

(Average Mass of Molded Article)

[0126] The weight of each of 30 molded foam articles having dimensions of 150 mm ? 150 mm ?thickness 2.4 mm, or 250 mm ?360 mm ?thickness 3 mm, was measured, and the average weight was calculated.

(Standard Deviation of Molded Article)

[0127] Using the above average weight of the molded article, the standard deviation was calculated using the following formula.

[Numerical formula 1]

$$s = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - \bar{x})^2}$$

n: total number of data
x_i: weight of individual molded article
x: average weight of molded articles

(Evaluation of Fluctuation in Molded Article Weight)

[0128] The fluctuation in the molded article weight was evaluated against the following criteria.

A: when the standard deviation of the molded article weight is less than 0.15%
B: when the standard deviation of the molded article weight is at least 0.15% but less than 0.25%
C: when the standard deviation of the molded article weight is at least 0.25% but less than 0.35%
D: when the standard deviation of the molded article weight is 0.35% or greater

(Naming of Unfoamed Molded Articles)

[0129] In contrast to a molded foam article, an unfoamed molded article produced using a production method in which a supercritical fluid is not injected during molding and no foaming occurs is defined a "solid molded article".

(Average Flexural Strength of Molded Article)

[0130] The average flexural strength of each of the solid molded articles disclosed in Examples 10 to 17 was determined using test pieces (MD direction: 140 mm ?TD direction: 10 mm) prepared by cutting 140 mm along the resin flow direction (hereinafter also referred to as the MD direction) and 10 mm along the direction perpendicular to the flow direction (hereinafter also referred to as the TD direction) from the central portion of a solid molded article of 150 mm ?150 mm ?thickness 3 mm, or 150 mm ?150 mm ?thickness 4 mm, by conducting measurements in accordance with ISO 178 using an n value of 3, and then calculating the average value.

[0131] The average flexural strength of the solid molded article disclosed in Comparative Example 6 was determined using solid molded articles formed as ISO 3167 A-type dumbbell test pieces (shape of parallel portion: 80 mm ?10 mm ?thickness 4 mm), by conducting measurements in accordance with ISO 178 using an n value of 3, and then calculating the average value.

[0132] The average flexural strength of each of the molded foam articles disclosed in Examples 18 to 25 and Comparative Examples 7 and 8 was determined using test pieces prepared by cutting a shape of 140 mm along the MD direction ?10 mm along the TD direction from the central portion of a molded foam article of 150 mm ?150 mm ? thickness 3 mm, or 150 mm ?150 mm ?thickness 4 mm, by conducting measurements in accordance with ISO 178 using an n value of 3, and then calculating the average value.

(Measurement of Specific Gravity of Molded Article)

[0133] The specific gravity of each solid molded article and molded foam article was measured using the same shaped test pieces as the test pieces used for measurement of the average flexural strength, by measuring the weight and volume using an n value of 3, determining the average value for both the weight and the volume, and then calculating

the specific gravity using the following formula.

$$\text{Specific gravity of molded article} = (\text{weight of test piece}) / (\text{volume of test piece})$$

(Weight Reduction Ratio for Molded Foam Article)

[0134] The weight reduction ratio for each molded foam article was calculated from the specific gravity of the molded foam article and the specific gravity of the solid molded article using the following formula.

$$\text{Weight reduction ratio for molded foam article} = (\text{specific gravity of solid molded article} - \text{specific gravity of molded foam article}) / (\text{specific gravity of solid molded article}) \times 100$$

(Strength Retention Ratio for Average Flexural Strength of Molded Foam Article)

[0135] The strength retention ratio for the average flexural strength of the molded foam article was calculated from the average flexural strength of the solid molded article and the average flexural strength of the molded foam article using the following formula.

$$\text{Strength retention ratio for average flexural strength of molded foam article} = (\text{average flexural strength of molded foam article}) / (\text{average flexural strength of solid molded article}) \times 100$$

(Ratio of Strength Retention Ratio for Average Flexural Strength Relative to Weight Reduction Ratio for Molded Foam Article (Ratio A))

[0136] The ratio of the strength retention ratio for the average flexural strength relative to the weight reduction ratio for the molded foam article was deemed "ratio A". The ratio A was calculated using the following formula.

$$\text{Ratio A} = (100 - \text{strength retention ratio for average flexural strength of molded foam article (\%)}) / (\text{weight reduction ratio for molded foam article (\%)})$$

(Difference in Ratio A between Molded Foam Article of Thickness 4 mm and Molded Foam Article of Thickness 3 mm)

[0137] The difference in the ratio A between a molded foam article of thickness 4 mm and a molded foam article of thickness 3 mm was calculated using the following formula.

$$\text{Difference in ratio A between molded foam article of thickness 4 mm and molded foam article of thickness 3 mm} = (\text{ratio A for molded foam article of thickness 4 mm}) - (\text{ratio A for molded foam article of thickness 3 mm})$$

(Evaluation of Size of Difference in Ratio A between Molded Foam Article of Thickness 4 mm and Molded Foam Article of Thickness 3 mm)

[0138] The size of the difference in the ratio A values was evaluated against the following criteria.

A: when the difference in ratio A values is at least 0.02
B: when the difference in ratio A values is at least 0.00 but less than 0.02
C: when the difference in ratio A values is less than 0.00.

<Production Example 1>

Production Method for LCP1

[0139] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with 6-hydroxy-2-naphthoic acid (1,034.99 g, 5.5 mol), 2,6-naphthalenedicarboxylic acid (378.33 g, 1.75 mol), terephthalic acid (83.07 g, 0.5 mol), hydroquinone (272.52 g, 2.475 mol, a 0.225 molar excess relative to the total amount of 2,6-naphthalenedicarboxylic acid and terephthalic acid), acetic anhydride (1,226.87 g, 12 mol), and 1-methylimidazole (0.17 g) as a catalyst, and following replacement of the gas inside the reactor with nitrogen gas, the temperature was raised from room temperature to 145°C over a period of 15 minutes while stirring the contents under a stream of nitrogen gas, and the mixture was then refluxed at 145°C for one hour. Subsequently, the temperature was raised from 145°C to 310°C over a period of 3.5 hours, while by-product acetic acid and unreacted acetic anhydride were removed by distillation, and after holding the temperature at 310°C for 3 hours, the contents were extracted and cooled to room temperature.

[0140] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a solid phase polymerization by heating, under an atmosphere of nitrogen, from room temperature to 250°C over a period of one hour and then from 250°C to 310°C over a period of 10 hours, and then holding the temperature at 300°C for 6 hours. Following the solid phase polymerization, the product was cooled to obtain a powdered liquid crystal polyester. The flow start temperature of this liquid crystal polyester was 303°C. The liquid crystal polyester obtained in this manner was termed LCP1.

[0141] If the total amount of all the repeating units that constitute LCP1 is deemed 100 mol%, then LCP1 had 55 mol% of a repeating unit (1) in which Ar^1 was a 2,6-naphthylene group, 17.5 mol% of a repeating unit (2) in which Ar^2 was a 2,6-naphthylene group, 5 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, and 22.5 mol% of a repeating unit (3) in which Ar^3 was a 1,4-phenylene group.

<Production Example 2>

Production Method for LCP2

[0142] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with 6-hydroxy-2-naphthoic acid (1,034.99 g, 5.5 mol), 2,6-naphthalenedicarboxylic acid (378.33 g, 1.75 mol), terephthalic acid (83.07 g, 0.5 mol), hydroquinone (272.52 g, 2.475 mol, a 0.225 molar excess relative to the total amount of 2,6-naphthalenedicarboxylic acid and terephthalic acid), acetic anhydride (1,226.87 g, 12 mol), and 1-methylimidazole (0.17 g) as a catalyst, and following replacement of the gas inside the reactor with nitrogen gas, the temperature was raised from room temperature to 145°C over a period of 15 minutes while stirring the contents under a stream of nitrogen gas, and the mixture was then refluxed at 145°C for one hour. Subsequently, the temperature was raised from 145°C to 310°C over a period of 3.5 hours, while by-product acetic acid and unreacted acetic anhydride were removed by distillation, and after holding the temperature at 310°C for 3 hours, the contents were extracted and cooled to room temperature.

[0143] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a solid phase polymerization by heating, under an atmosphere of nitrogen, from room temperature to 250°C over a period of one hour and then from 250°C to 310°C over a period of 10 hours, and then holding the temperature at 310°C for 6 hours. Following the solid phase polymerization, the product was cooled to obtain a powdered liquid crystal polyester. The flow start temperature of this liquid crystal polyester was 324°C. The liquid crystal polyester obtained in this manner was termed LCP2.

[0144] If the total amount of all the repeating units that constitute LCP2 is deemed 100 mol%, then LCP2 had 55 mol% of a repeating unit (1) in which Ar^1 was a 2,6-naphthylene group, 17.5 mol% of a repeating unit (2) in which Ar^2 was a 2,6-naphthylene group, 5 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, and 22.5 mol% of a repeating unit (3) in which Ar^3 was a 1,4-phenylene group.

<Production Example 3>

Production Method for LCP3

[0145] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with 6-hydroxy-2-naphthoic acid (1,034.99 g, 5.5 mol), 2,6-naphthalenedicarboxylic acid (378.33 g, 1.75 mol), terephthalic acid (83.07 g, 0.5 mol), hydroquinone (272.52 g, 2.475 mol, a 0.225 molar excess relative to the total amount of 2,6-naphthalenedicarboxylic acid and terephthalic acid), acetic anhydride (1,226.87 g, 12 mol), and 1-methylimidazole (0.17 g) as a catalyst, and following replacement of the gas inside the reactor with nitrogen gas, the temperature was raised from room temperature to 145°C over a period of 15 minutes while stirring the contents under a stream of nitrogen gas, and the mixture was then refluxed at 145°C for one hour. Subsequently, the temperature was raised from 145°C to 310°C over a period of 3.5 hours, while by-product acetic acid and unreacted acetic anhydride were removed by distillation, and after holding the temperature at 310°C for 3 hours, the contents were extracted and cooled to room temperature.

[0146] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a solid phase polymerization by heating, under an atmosphere of nitrogen, from room temperature to 250°C over a period of one hour and then from 250°C to 310°C over a period of 10 hours, and then holding the temperature at 310°C for 10 hours. Following the solid phase polymerization, the product was cooled to obtain a powdered liquid crystal polyester. The flow start temperature of this liquid crystal polyester was 334°C. The liquid crystal polyester obtained in this manner was termed LCP3.

[0147] If the total amount of all the repeating units that constitute LCP3 is deemed 100 mol%, then LCP3 had 55 mol% of a repeating unit (1) in which Ar^1 was a 2,6-naphthylene group, 17.5 mol% of a repeating unit (2) in which Ar^2 was a 2,6-naphthylene group, 5 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, and 22.5 mol% of a repeating unit (3) in which Ar^3 was a 1,4-phenylene group.

<Production Example 4>

Production Method for LCP4

[0148] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with p-hydroxybenzoic acid (994.5 g, 7.2 mol), terephthalic acid (299.1 g, 1.8 mol), isophthalic acid (99.7 g, 0.6 mol), 4,4'-dihydroxybiphenyl (446.9 g, 2.4 mol), acetic anhydride (1,347.6 g, 13.2 mol), and 1-methylimidazole (0.194 g), the temperature was raised from room temperature to 150°C over a period of 30 minutes while the contents were stirred under a stream of nitrogen gas, and the mixture was then refluxed at 150°C for one hour. Subsequently, a further 0.9 g of 1-methylimidazole was added, the temperature was raised to 320°C over a period of 2 hours and 50 minutes while by-product acetic acid and unreacted acetic anhydride were removed by distillation, the temperature was then held at 320°C until an increase in torque was noticed, and the contents were then extracted from the reactor and cooled to room temperature.

[0149] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a solid phase polymerization by heating, under an atmosphere of nitrogen gas, from room temperature to 250°C over a period of one hour and then from 250°C to 285°C over a period of 5 hours, and then holding the temperature at 285°C for 3 hours. Following the solid phase polymerization, the product was cooled to obtain a powdered liquid crystal polyester. The flow start temperature of this liquid crystal polyester was 327°C. The liquid crystal polyester obtained in this manner was termed LCP4.

[0150] If the total amount of all the repeating units that constitute LCP4 is deemed 100 mol%, then LCP4 had 60 mol% of a repeating unit (1) in which Ar^1 was a 1,4-phenylene group, 15 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, 5 mol% of a repeating unit (2) in which Ar^2 was a 1,3-phenylene group and 20 mol% of a repeating unit (3) in which Ar^3 was a 4,4'-biphenylylene group.

<Production Example 5>

Production Method for LCP5

[0151] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with p-hydroxybenzoic acid (994.5 g, 7.2 mol), terephthalic acid (299.1 g, 1.8 mol), isophthalic acid (99.7 g, 0.6 mol), 4,4'-dihydroxybiphenyl (446.9 g, 2.4 mol), acetic anhydride (1,347.6 g, 13.2 mol), and 1-methylimidazole (0.194 g) as a catalyst, the resultant mixture was stirred at room temperature for 15 minutes while the inside of the reactor was flushed thoroughly with nitrogen gas, and the temperature was then raised under continuous stirring.

Once the internal temperature reached 145°C, stirring was continued at the same temperature for one hour. Subsequently, the temperature was further raised over a period of 2 hours and 50 minutes while by-product acetic acid and unreacted acetic anhydride were removed by distillation, the temperature was then held at 320°C until an increase in torque was noticed, and the contents were then extracted from the reactor and cooled to room temperature.

[0152] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a solid phase polymerization by heating, under an atmosphere of nitrogen, from room temperature to 250°C over a period of one hour and then from 250°C to 285°C over a period of 5 hours, and then holding the temperature at 285°C for 3 hours. Following the solid phase polymerization, the product was cooled to obtain a powdered liquid crystal polyester. The flow start temperature of this liquid crystal polyester was 327°C. The liquid crystal polyester obtained in this manner was termed LCP5.

[0153] If the total amount of all the repeating units that constitute LCP5 is deemed 100 mol%, then LCP5 had 60 mol% of a repeating unit (1) in which Ar^1 was a 1,4-phenylene group, 15 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, 5 mol% of a repeating unit (2) in which Ar^2 was a 1,3-phenylene group and 20 mol% of a repeating unit (3) in which Ar^3 was a 4,4'-biphenylylene group.

<Production Example 6>

Production Method for LCP6

[0154] A reactor fitted with a stirring device, a torque meter, a nitrogen gas inlet tube, a thermometer and a reflux condenser was charged with p-hydroxybenzoic acid (994.5 g, 7.2 mol), 4,4'-dihydroxybiphenyl (446.9 g, 2.4 mol), terephthalic acid (358.8 g, 2.16 mol), isophthalic acid (39.9 g, 0.24 mol), acetic anhydride (1,347.6 g, 13.2 mol), and 1-methylimidazole (0.194 g) as a catalyst, the resultant mixture was stirred at room temperature for 15 minutes while the inside of the reactor was flushed thoroughly with nitrogen gas, and the temperature was then raised under continuous stirring. Once the internal temperature reached 145°C, stirring was continued at the same temperature for one hour. Subsequently, the temperature was further raised over a period of 2 hours and 50 minutes while by-product acetic acid and unreacted acetic anhydride were removed by distillation, the temperature was then held at 320°C until an increase in torque was noticed, and the contents were then extracted from the reactor and cooled to room temperature.

[0155] The obtained solid matter was ground to a particle size of about 0.1 to 1 mm using a grinder, thus obtaining a powdered prepolymer. Subsequently, this prepolymer was subjected to a polymerization in the solid phase by heating, under an atmosphere of nitrogen, from room temperature to 250°C over a period of one hour and then from 250°C to 300°C over a period of 5 hours, and then holding the temperature at 300°C for 3 hours. The flow start temperature of the thus obtained polyester was 361 °C. The liquid crystal polyester obtained in this manner was termed LCP3.

[0156] If the total amount of all the repeating units that constitute LCP6 is deemed 100 mol%, then LCP6 had 60 mol% of a repeating unit (1) in which Ar^1 was a 1,4-phenylene group, 18 mol% of a repeating unit (2) in which Ar^2 was a 1,4-phenylene group, 2 mol% of a repeating unit (2) in which Ar^2 was a 1,3-phenylene group and 20 mol% of a repeating unit (3) in which Ar^3 was a 4,4'-biphenylylene group.

<Production of Resin Compositions, Examples 1 to 9, Comparative Examples 1 to 5>

«Examples 1, 2, 4, 5?

[0157] The abovementioned LCP2, LCP4 or LCP5 was mixed as a liquid crystal resin under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component was fed into the extruder from a feeder with the cylinder temperature set to 340°C, and was subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition.

[0158] Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 360°C, while nitrogen in a supercritical state was introduced under the conditions shown in Table 1. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 150 mm ?150 mm ?thickness 1.2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 2.4 mm).

<<Comparative Example 1>>

[0159] The abovementioned LCP5 was mixed as a liquid crystal resin under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component was fed into the extruder from a feeder with the cylinder temperature set to 340°C, and was subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition.

[0160] Using a fully electric molding machine J450AD manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit that did not have a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM SII TRJ-30-A, manufactured by Trexel, Inc., recorded as "Device A" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 360°C, while nitrogen in a supercritical state (a supercritical fluid) was introduced under the conditions shown in Table 1. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 250 mm ?360 mm ?thickness 3 mm, and using the core-back method, and attempt was made to produce a molded foam article having a flat shape (250 mm ?360 mm ?thickness 6 mm), but the amount introduced of the supercritical fluid could not be stabilized, fluctuations occurred in the resin pressure during the melt-kneading in the molding machine, the supercritical fluid could not be introduced in a stable manner at the desired settings, and even upon core-back expansion of the mold, regions occurred in which foaming did not occur as designed, making it impossible to obtain the desired molded foam article.

<<Comparative Example 2>>

[0161] The abovementioned LCP1 was mixed as a liquid crystal resin under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component was fed into the extruder from a feeder with the cylinder temperature set to 320°C, and was subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition.

[0162] Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 330°C, while nitrogen in a supercritical state (a supercritical fluid) was introduced under the conditions shown in Table 1. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 150 mm ?150 mm ?thickness 1.2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 2.4 mm).

[0163] In the molded foam article of Comparative Example 2, because the LCP had a low melt tension and the melt viscosity of the resin composition was also too low, not only did the gas bubbles coalesce during foaming, causing a deterioration in the foamed state inside the molded article, but fluctuations in the weight of the molded articles also increased.

<<Comparative example 3>>

[0164] The abovementioned LCP6 was mixed as a liquid crystal resin under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component was fed into the extruder from a feeder with the cylinder temperature set to 370°C, and was subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition.

[0165] Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 380°C, while nitrogen in a supercritical state (a supercritical fluid) was introduced under the conditions shown in Table 1. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 150 mm ?150 mm ?thickness 1.2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 2.4 mm).

«Examples 6 and 7, Comparative Examples 3 and 4>>

[0166] The abovementioned LCP3 was mixed as a liquid crystal resin under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component was fed into the extruder from a feeder with the cylinder temperature set to 350°C, and was subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition. Using a fully electric molding machine J11OAD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 360°C, while nitrogen in a supercritical state (a supercritical fluid) was introduced under the conditions shown in Table 1, and the melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 150 mm ?150 mm ?thickness 1.2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 2.4 mm).

[0167] In the molded foam articles of Comparative Examples 3 and 4, because the amount introduced of the supercritical fluid was too large, not only did the gas bubbles coalesce during foaming, causing a deterioration in the foamed state inside the molded articles, but fluctuations in the weight of the molded articles also increased.

<<Examples 8 and 9, Comparative Example 5>>

[0168] The abovementioned LCP2 or LCP5 as a liquid crystal resin, and glass fiber were mixed under the conditions shown in Table 1. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.) and a water-sealed vacuum pump (SW-25 manufactured by Shinko Seiki Co., Ltd.), the resin component and the inorganic filler were fed into the extruder from a feeder with the cylinder temperature set to 350°C, and were subjected to melt-kneading by the screws with an inserted kneading block, while degassing was conducted through a vacuum vent. The discharged strand was cut to obtain pellets of the resin composition. Using a fully electric molding machine J 1 lOAD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 1), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 360°C, while nitrogen in a supercritical state (a supercritical fluid) was introduced under the conditions shown in Table 1, and the melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 120°C into a mold having a cavity shape of 150 mm ?150 mm ?thickness 1.2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 2.4 mm).

[0169] In the molding of the molded foam article of Comparative Example 5, although the amount introduced of the supercritical fluid was within a range from at least 0.1 parts by mass to not more than 0.3 parts by mass, because the specified amount of the supercritical fluid was only introduced at a frequency of once per three repetitions of plasticization metering (meaning the supercritical fluid was introduced at a frequency of once per 3 shots), the state of dispersion of the supercritical fluid impregnated into the melted resin inside the molding machine cylinder lost uniformity, and the foamed state inside the molded articles deteriorated.

[0170] For Examples 1 to 9 and Comparative Examples 1 to 5, the molding conditions, the LCP melt tension, the resin composition viscosity, the void ratio, the foamed state inside the molded article, the average weight of the molded bodies, the standard deviation of the weight of the molded articles, and an evaluation of the fluctuation in the weight of the molded articles are shown in Table 1. In Table 1, the symbols used have the following meanings.

- cGF: chopped glass fiber CS3J-260S (manufactured by Nitto Boseki Co., Ltd.)
- mGF: milled glass fiber EFH75-01 (manufactured by Central Glass Fiber Co., Ltd.)

[Table 1]

Material		Units	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
LCP	LCP1	parts by mass											100			
	LCP2	parts by mass				100	100				55					55
	LCP3	parts by mass						100	100					100	100	
	LCP4	parts by mass	100													
	LCP5	parts by mass		100						60		100				
	LCP6	parts by mass			100						45					45
cGF (short glass fiber)	CS3J-260S	parts by mass														
mGF (milled glass fiber)	EFH75-01	parts by mass								40						
Molding method			Foam molding													
Supercritical fluid injection device			Device B									Device A	Device B			
Type of supercritical fluid			Nitrogen													
Supercritical fluid injection frequency			Injection every repetition													intermittent injection (once per 3 shots)
Supercritical fluid average injection amount (injection amount per 100 parts by mass of LCP)		parts by mass	0.2	0.2	0.2	0.2	0.3	0.1	0.2	0.2	0.3	0.1	0.2	0.4	0.7	0.3
Melt tension of neat LCP		mN	5	13	71	14	14	52	52	13	14	13	3	52	52	14
Melt viscosity of resin composition		Pa·s	230	650	1600	410	410	4000	4000	3500	3400	650	20	4000	4000	3400
Void ratio		%	1.35	0.95	0.15	0.94	1.24	0.10	0.56	0.33	0.26	Molded foam bodies not obtained	4.66	3.41	3.27	1.63
Foamed state inside molded articles			C	B	A	B	C	A	B	A	A		D	D	D	D
Average weight of molded articles		g	57.17	54.76	52.63	48.52	47.52	49.29	47.45	68.82	61.00		58.01	42.44	43.60	64.23
Standard deviation of weight of molded articles		g	0.28	0.25	0.13	0.04	0.26	0.05	0.24	0.27	0.08		0.39	0.40	0.42	0.17
Evaluation of fluctuation in weight of molded articles			C	C	A	A	C	A	B	C	A		D	D	D	B

[0171] As is evident from the results shown above in Table 1, Examples 1 to 9 which applied the present invention all exhibited a favorable foamed state inside the molded articles, and were able to produce molded foam bodies having little fluctuation in the weight of the molded articles.

[0172] In contrast, Comparative Examples 1 to 5 which did not apply the present invention not only all exhibited a poor foamed state inside the molded articles, but in some cases also suffered from a larger fluctuation in the weight of the molded articles.

<Production of Resin Compositions, Examples 10 to 25, Comparative Examples 6 to 8>

<<Examples 10 to 25>>

[0173] LCP2 produced in Production Example 2 and glass fiber were mixed in the blending ratios shown in Tables 2 and 3. Specifically, using a twin-screw extruder (PCM-30HS manufactured by Ikegai, Ltd.), the resin components were fed into the extruder from a feeder with the cylinder temperature set to 340°C, and were subjected to melt-kneading by the screws with an inserted kneading block. The discharged strand was cut to obtain pellets of the resin composition.

<<Production of Solid Molded Articles of Examples 10 to 17>>

[0174] Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., the pellets produced using the method described above were used to produce solid molded articles. When producing the solid molded articles, no supercritical fluid injection was performed. The resin composition was heated and metered inside the cylinder with the temperature set to 360°C, and the melted resin was injected at a temperature setting of 80°C into a mold having a cavity shape of 150 mm ? 150 mm ?thickness 3 mm or 150 mm ?150 mm ?thickness 4 mm to obtain a solid molded body having a flat shape.

<<Production of Molded Foam Articles of Examples 18 to 25>>

[0175] Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 2), the resin composition of the pellets produced using the above method was heated and metered inside the cylinder with the temperature set to 360°C, while nitrogen in a supercritical state was introduced under the conditions shown in Table 2. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 80°C into a mold having a cavity shape prior to core-back of 150 mm ?150 mm ?thickness 1.5 mm or 150 mm ?150 mm ?thickness 2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ?150 mm ?thickness 3 mm or 150 mm ?150 mm ?thickness 4 mm).

<<Production of Solid Molded Article of Comparative Example 6>>

[0176] A polyamide 66 (hereinafter sometimes abbreviated as PA66) resin composition (Ultramid A3WG6 (a blended product containing 30% by mass of glass fiber)) was molded as a polyamide resin under the conditions shown in Table 2. Using a fully electric molding machine PNX40-5A manufactured by Nissei Plastic Industrial Co., Ltd., the resin composition was heated and metered inside the cylinder with the temperature set to 280°C, and the melted resin was injected at a temperature setting of 80°C into a mold having a cavity shape corresponding with an ISO 3167 A-type dumbbell test piece (shape of parallel portion: 80 mm ?10 mm ?thickness 4 mm) to obtain a solid molded article.

<<Production of Molded Foam Articles of Comparative Examples 7 and 8>>

[0177] A PA66 resin composition (Ultramid A3WG6 (a blended product containing 30% by mass of glass fiber)) was molded as a polyamide resin under the conditions shown in Table 3. Using a fully electric molding machine J110AD-180H manufactured by The Japan Steel Works, Ltd., and a supercritical fluid production unit having a feedback control function for the amount introduced of the supercritical fluid (SCF SYSTEM T-100J, manufactured by Trexel, Inc., recorded as "Device B" in Table 3), the resin composition was heated and metered inside the cylinder with the temperature set to 280°C, while nitrogen in a supercritical state was introduced under the conditions shown in Table 2. The melted resin containing the dissolved supercritical fluid was injected at a temperature setting of 80°C into a mold having a cavity shape prior to core-back of 150 mm ?150 mm ?thickness 1.5 mm or 150 mm ?150 mm ?thickness 2 mm, and the core-back method was used to obtain a molded foam body having a flat shape (150 mm ? 150 mm ?thickness 3 mm or 150 mm ?150 mm ?thickness 4 mm).

[0178] For the above Examples 10 to 25 and Comparative Examples 6 to 8, the molding conditions, the average flexural strength of the molded articles, the weight reduction ratio for the molded foam article, the strength retention ratio for the average flexural strength of the molded foam articles, the ratio of the strength retention ratio for the average

flexural strength relative to the weight reduction ratio for the molded foam article (ratio A), the difference in the ratio A between a molded foam article of thickness 4 mm and a molded foam article of thickness 3 mm, and an evaluation of the size of the difference in the ratio A between a molded foam article of thickness 4 mm and a molded foam article of thickness 3 mm are shown in Tables 2 and 3. In Tables 2 and 3, the symbol used has the following meaning.

- cGF: chopped glass fiber CS3J-260S (manufactured by Nitto Boseki Co., Ltd.)

[0179]

[Table 2]

	Item	Units	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Comparative Example 6
Materials	LCP2	parts by mass	100	100	90	90	80	80	70	70	100
	PA66 resin composition	parts by mass	-	-	-	-	-	-	-	-	-
	cGF	parts by mass	-	-	10	10	20	20	30	30	-
Molding	Molding method	-	Solid molding								
	Supercritical fluid injection device	-	-	-	-	-	-	-	-	-	-
	Type of supercritical fluid	-	-	-	-	-	-	-	-	-	-
	Supercritical fluid average injection amount (injection amount per 100 parts by mass of LCP)	parts by mass	-	-	-	-	-	-	-	-	-

(continued)

	Item	Units	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Comparative Example 6
Evaluations	Thickness of molded article	mm	4	3	4	3	4	3	4	3	4
	Specific gravity of molded article	g/cm^3	1.36	1.38	1.41	1.43	1.48	1.50	1.52	1.51	1.33
	Average flexural strength of molded article	MPa	137	154	138	148	137	152	137	147	218
	Weight reduction ratio for molded foam article	%	-	-	-	-	-	-	-	-	-
	Strength retention ratio for average flexural strength of molded foam article	%	-	-	-	-	-	-	-	-	-
	Ratio of the strength retention ratio for the average flexural strength relative to the weight reduction ratio for molded foam article (ratio A)	-	-	-	-	-	-	-	-	-	-
	Difference in ratio A between molded foam article of thickness 4 mm and molded foam article of thickness 3 mm	-	-	-	-	-	-	-	-	-	-
	Evaluation of size of difference in ratio A between molded foam article of thickness 4 mm and molded foam article of thickness 3 mm	-	-	-	-	-	-	-	-	-	-

[0180]

[Table 3]

	Item	Units	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Comparative Example 7	Comparative Example 8
Materials	LCP2	parts by mass	100	100	90	90	80	80	70	70	100	100
	PA66 resin composition	parts by mass	-	-	-	-	-	-	-	-	-	-
	cGF	parts by mass	-	-	10	10	20	20	30	30	-	-
Molding	Molding method	-	Foam molding									
	Supercritical fluid injection device	-	Device B									
	Type of supercritical fluid	-	Nitrogen									
	Supercritical fluid average injection amount (injection amount per 100 parts by mass of LCP)	parts by mass	0.3	03	0.3	0.3	0.3	0.3	0.3	0.3	0.7	0.7
	Thickness of molded article	mm	4	3	4	3	4	3	4	3	4	3
	Specific gravity of molded article	g/cm^3	0.72	0.73	0.72	0.73	0.75	0.78	0.81	0.85	0.68	0.77

(continued)

	Item	Units	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Comparative Example 7	Comparative Example 8
Evaluations	Average flexural strength of molded article	MPa	69	78	76	86	81	95	86	97	58	79
	Weight reduction ratio for molded foam article	%	47.1	47.1	48.9	49.0	49.3	48.0	46.7	43.7	48.9	42.1
	Strength retention ratio for average flexural strength of molded foam article	%	50.4	50.6	55.1	58.1	59.1	62.5	62.8	66.0	26.6	36.2
	Ratio of the strength retention ratio for the average flexural strength relative to the weight reduction ratio for molded foam article (ratio A)	-	1.055	1.048	0.918	0.856	0.829	0.781	0.797	0.778	1.502	1.514

(continued)

	Item	Units	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24	Example 25	Comparative Example 7	Comparative Example 8
	Difference in ratio Λ between molded foam article of thickness 4 mm and molded foam article of thickness 3 mm	-	-	0.007	-	0.062	-	0.047	-	0.019	-	-0.013
	Evaluation of size of difference in ratio A between molded foam article of thickness 4 mm and molded foam article of thickness 3 mm	-	-	B	-	A	-	A	-	B	-	C

[0181] As is evident from the results shown above in Tables 2 and 3, Examples 18 to 25 which applied the present invention all exhibited a tendency for an improvement in the strength retention ratio as the thickness of the molded foam article was reduced.

[0182] In contrast, Comparative Examples 7 and 8 did not exhibit a tendency for an improvement in the strength retention ratio even when the thickness of the molded foam article was reduced.

INDUSTRIAL APPLICABILITY

[0183] The present invention can provide a method for producing molded foam articles that enables a resin composition containing an LCP to be foamed uniformly, and enables suppression of fluctuations in the weight of the molded foam articles, and can also provide molded foam articles, and is therefore extremely useful industrially.

EXPLANATION OF REFERENCES

[0184]

1: Injection molding machine
11: Main body
12: Mold
21: Introduction device
111: Cylinder
112: Screw
113: Hopper
211: Gas cylinder
212: Pressurizer
213: Control valve

Claims

1. A method for producing molded foam articles that molds molded foam articles continuously, **characterized in that** the method comprises continuously repeating step 1, step 2, step 3 and step 4 described below in this order, wherein

step 1 comprises melting a resin composition that includes a liquid crystal polyester, wherein the amount of the liquid crystal polyester, relative to the total mass of the resin composition, is greater than 30% by mass but not more than 100% by mass,
step 2 comprises introducing, with an introduction device, a supercritical fluid that is unreactive, in a supercritical state, with the liquid crystal polyester, and is a gas at normal temperature and normal pressure, into the resin composition in an amount of at least 0.1 parts by mass but not more than 0.3 parts by mass per 100 parts by mass of the liquid crystal polyester, and then melt-kneading a resultant mixture,
step 3 comprises injecting the melt-kneaded resin composition containing the supercritical fluid into a mold, and
step 4 comprises conducting foaming by lowering at least one of a pressure and a temperature of the supercritical fluid contained in the resin composition to a value below a critical point of the supercritical fluid, and
the method further comprises measuring an amount introduced of the supercritical fluid, and performing feedback control of the amount introduced of the supercritical fluid based on a measurement result; and
the liquid crystal polyester has a melt tension at a temperature 20°C higher than a flow start temperature of at least 5 mN but not more than 100 mN, wherein the melt tension is measured in accordance with the description.

2. The method for producing molded foam articles according to claim 1, wherein the liquid crystal polyester has a repeating unit represented by general formula (1) shown below, a repeating unit represented by general formula (2) shown below, and a repeating unit represented by general formula (3) shown below:

(1)

$$-O-Ar^1-CO-$$

(2)

-CO-Ar^2-CO-

(3)

-X-Ar^3-Y-

wherein

Ar^1 represents a phenylene group, naphthylene group or biphenylylene group;
Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below;
X and Y each independently represent an oxygen atom or an imino group; and
at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group,

(4)

-Ar^4-Z-Ar^5-

wherein
Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group.

3. The method for producing molded foam articles according to claim 1 or 2, wherein following injection of the melt-kneaded resin composition containing the supercritical fluid into the mold, the resin composition containing the supercritical fluid is foamed using a core-back method.

4. The method for producing molded foam articles according to any one of claims 1 to 3, wherein the supercritical fluid is nitrogen.

5. The method for producing molded foam articles according to any one of claims 1 to 4, wherein the resin composition comprises an inorganic filler in an amount exceeding 0 parts by mass but not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester.

6. The method for producing molded foam articles according to any one of claims 1 to 5, wherein a viscosity of the resin composition at a temperature 20°C higher than a flow start temperature is at least 200 Pa- s but not more than 5,000 Pa·s, wherein the viscosity is measured in accordance with the description.

7. A molded foam article that is molded from a foaming material and a resin composition, wherein

the resin composition comprises a liquid crystal polyester containing a repeating unit represented by general formula (1) shown below, a repeating unit represented by general formula (2) shown below and a repeating unit represented by general formula (3) shown below, and also comprises an inorganic filler,
an amount of the inorganic filler exceeds 0 parts by mass but is not more than 100 parts by mass per 100 parts by mass of the liquid crystal polyester,

(1)

-O-Ar^1-CO-

(2)

-CO-Ar^2-CO-

(3)

-X-Ar^3-Y-

wherein

Ar^1 represents a phenylene group, naphthylene group or biphenylylene group;
Ar^2 and Ar^3 each independently represent a phenylene group, naphthylene group, biphenylylene group, or a group represented by general formula (4) shown below;
X and Y each independently represent an oxygen atom or an imino group; and
at least one hydrogen atom in Ar^1, Ar^2 and Ar^3 may be independently substituted with a halogen atom, an alkyl group or an aryl group,

(4)

$$-Ar^4-Z-Ar^5-$$

wherein
Ar^4 and Ar^5 each independently represent a phenylene group or a naphthylene group; and Z represents an oxygen atom, sulfur atom, carbonyl group, sulfonyl group or alkylidene group;

characterized in that
the resin composition has a viscosity at a temperature 20°C higher than a flow start temperature of the resin composition of at least 200 Pa·s but not more than 5,000 Pa·s, and
the liquid crystal polyester has a melt tension at a temperature 20°C higher than a flow start temperature of the liquid crystal polyester of at least 5 mN but not more than 100 mN,
wherein the viscosity and the melt tension are measured in accordance with the description.

8. The molded foam article according to claim 7, having a thin-wall portion with a thickness of 4.0 mm or less.

Patentansprüche

1. Ein Verfahren zur Herstellung von Schaumstoff-Formgegenständen, das Schaumstoff-Formgegenstände kontinuierlich formt, **dadurch gekennzeichnet, dass** das Verfahren das kontinuierliche Wiederholen von Schritt 1, Schritt 2, Schritt 3 und Schritt 4, wie unten beschrieben, in dieser Reihenfolge, umfasst, wobei

Schritt 1 das Schmelzen einer Harzzusammensetzung umfasst, die einen Flüssigkristall-Polyester enthält, wobei die Menge des Flüssigkristall-Polyesters, bezogen auf die Gesamtmasse der Harzzusammensetzung, größer als 30 Massen-%, aber nicht mehr als 100 Massen-%, ist,
Schritt 2 das Einführen, mit einer Einführungsvorrichtung, eines überkritischen Fluids, das in einem überkritischen Zustand mit dem Flüssigkristall-Polyester nicht reaktiv ist und bei Normaltemperatur und Normaldruck ein Gas ist, in die Harzzusammensetzung in einer Menge von mindestens 0,1 Massenteilen, aber nicht mehr als 0,3 Massenteilen, pro 100 Massenteile des Flüssigkristall-Polyesters, und anschließendes Schmelzkneten eines so erhaltenen Gemisches umfasst,
Schritt 3 das Einspritzen der schmelzgekneteten Harzzusammensetzung, enthaltend das überkritische Fluid, in eine Form umfasst, und
Schritt 4 das Durchführen des Schäumens durch Verringern von mindestens einem von einem Druck und einer Temperatur des in der Harzzusammensetzung enthaltenen überkritischen Fluids auf einen Wert unterhalb eines kritischen Punkts des überkritischen Fluids und
das Verfahren ferner das Messen einer eingeführten Menge des überkritischen Fluids und das Durchführen einer Feedback-Kontrolle der eingeführten Menge des überkritischen Fluids auf der Grundlage eines Messergebnisses umfasst; und
der Flüssigkristall-Polyester eine Schmelzspannung bei einer Temperatur, die 20°C höher ist als eine Fließbeginntemperatur, von mindestens 5 mN, aber nicht mehr als 100 mN, aufweist, wobei die Schmelzspannung gemäß der Beschreibung gemessen wird.

2. Das Verfahren zur Herstellung von Schaumstoff-Formgegenständen nach Anspruch 1, wobei der Flüssigkristall-Polyester eine sich wiederholende Einheit, dargestellt durch die unten stehende allgemeinen Formel (1), eine sich wiederholende Einheit, dargestellt durch die unten stehende allgemeinen Formel (2), und eine sich wiederholende Einheit, dargestellt durch unten stehende allgemeinen Formel (3), aufweist:

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

wobei

Ar^1 eine Phenylengruppe, Naphthylengruppe oder Biphenylylengruppe darstellt;
Ar^2 und Ar^3 jeweils unabhängig eine Phenylengruppe, eine Naphthylengruppe, eine Biphenylylengruppe oder eine Gruppe, dargestellt durch die unten stehende allgemeine Formel (4), darstellen;
X und Y jeweils unabhängig ein Sauerstoffatom oder eine Iminogruppe darstellen; und mindestens ein Wasserstoffatom in Ar^1, Ar^2 und Ar^3 unabhängig durch ein Halogenatom, eine Alkylgruppe oder eine Arylgruppe substituiert sein kann,

(4)

$$-Ar^4-Z-Ar^5-$$

wobei

Ar^4 und Ar^5 jeweils unabhängig eine Phenylengruppe oder eine Naphthylengruppe darstellen; und
Z ein Sauerstoffatom, ein Schwefelatom, eine Carbonylgruppe, eine Sulfonylgruppe oder eine Alkylidengruppe darstellt.

3. Das Verfahren zur Herstellung von Schaumstoff-Formgegenständen nach Anspruch 1 oder 2, wobei nach dem Einspritzen der schmelzgekneteten Harzzusammensetzung, die das überkritische Fluid enthält, in die Form, die Harzzusammensetzung, die das überkritische Fluid enthält, unter Verwendung eines Core-Back-Verfahrens geschäumt wird.

4. Das Verfahren zur Herstellung von Schaumstoff-Formgegenständen nach einem der Ansprüche 1 bis 3, wobei das überkritische Fluid Stickstoff ist.

5. Das Verfahren zur Herstellung von Schaumstoff-Formgegenständen nach einem der Ansprüche 1 bis 4, wobei die Harzzusammensetzung einen anorganischen Füllstoff in einer Menge von mehr als 0 Massenteilen, aber nicht mehr als 100 Massenteilen, pro 100 Massenteile des Flüssigkristall-Polyesters enthält.

6. Das Verfahren zur Herstellung von Schaumstoff-Formgegenständen nach einem der Ansprüche 1 bis 5, wobei eine Viskosität der Harzzusammensetzung bei einer Temperatur, die 20°C höher ist als die Fließbeginntemperatur, mindestens 200 Pa·s, aber nicht mehr als 5.000 Pa·s, beträgt, wobei die Viskosität gemäß der Beschreibung gemessen wird.

7. Ein Schaumstoff-Formgegenstand, der aus einem schäumenden Material und einer Harzzusammensetzung geformt ist, wobei

die Harzzusammensetzung einen Flüssigkristall-Polyester umfasst, der eine sich wiederholende Einheit, dargestellt durch die unten stehende allgemeine Formel (1), eine sich wiederholende Einheit, dargestellt durch die unten stehende allgemeine Formel (2), und eine sich wiederholende Einheit, dargestellt durch die unten stehende allgemeine Formel (3), enthält, und auch einen anorganischen Füllstoff umfasst,
eine Menge des anorganischen Füllstoffs 0 Massenteile übersteigt, aber nicht mehr als 100 Massenteile pro 100 Massenteile des Flüssigkristall-Polyesters beträgt,

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

wobei

Ar^1 eine Phenylengruppe, Naphthylengruppe oder Biphenylylengruppe darstellt;
Ar^2 und Ar^3 jeweils unabhängig eine Phenylengruppe, eine Naphthylengruppe, eine Biphenylylengruppe oder eine Gruppe, dargestellt durch die unten stehende allgemeine Formel (4), darstellen;
X und Y jeweils unabhängig ein Sauerstoffatom oder eine Iminogruppe darstellen; und mindestens ein Wasserstoffatom in Ar^1, Ar^2 und Ar^3 unabhängig durch ein Halogenatom, eine Alkylgruppe oder eine Arylgruppe substituiert sein kann,

(4)

$$-Ar^4-Z-Ar^5-$$

wobei

Ar^4 und Ar^5 jeweils unabhängig eine Phenylengruppe oder eine Naphthylengruppe darstellen; und
Z ein Sauerstoffatom, ein Schwefelatom, eine Carbonylgruppe, eine Sulfonylgruppe oder eine Alkylidengruppe darstellt;

dadurch gekennzeichnet, dass
die Harzzusammensetzung eine Viskosität bei einer Temperatur, die 20°C höher ist als eine Fließbeginntemperatur der Harzzusammensetzung, von mindestens 200 Pa·s, aber nicht mehr als 5.000 Pa s, beträgt, und der Flüssigkristall-Polyester eine Schmelzspannung bei einer Temperatur, die 20°C höher ist als die Fließbeginntemperatur des Flüssigkristall-Polyesters, von mindestens 5 mN, aber nicht mehr als 100 mN aufweist, wobei die Viskosität und die Schmelzspannung gemäß der Beschreibung gemessen werden.

8. Der Schaumstoff-Formgegenstand nach Anspruch 7, der einen dünnwandigen Abschnitt mit einer Dicke von 4,0 mm oder weniger aufweist.

Revendications

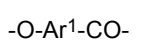
1. Méthode pour produire des articles expansés moulés qui moule des articles expansés moulés en continu, **caractérisée en ce que** la méthode comprend la répétition continue de l'étape 1, l'étape 2, l'étape 3 et l'étape 4 décrites ci-dessous dans cet ordre, dans laquelle

l'étape 1 comprend la fusion d'une composition de résine qui contient un polyester cristal liquide, dans laquelle la quantit?du polyester cristal liquide, par rapport ?la masse totale de la composition de résine, est supérieure ?30 % en masse mais non supérieure ? 100 % en masse,
l'étape 2 comprend l'introduction, au moyen d'un dispositif d'introduction, d'un fluide supercritique qui n'est pas réactif, ?l'état supercritique, avec le polyester cristal liquide, et qui est un gaz ?la température normale et sous la pression normale, dans la composition de résine en une quantit?d'au moins 0,1 partie en masse mais non supérieure ?0,3 partie en masse pour 100 parties en masse du polyester cristal liquide, et ensuite le malaxage ?l'état fondu du mélange résultant,
l'étape 3 comprend l'injection de la composition de résine malaxée ?l'état fondu contenant le fluide supercritique dans un moule, et

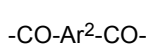
l'étape 4 comprend la mise en oeuvre d'une expansion par abaissement d'au moins l'une parmi la pression et la température du fluide supercritique contenu dans la composition de résine ?une valeur inférieure au point critique du fluide supercritique, et
la méthode comprend en outre la mesure de la quantit?introduite du fluide supercritique, et la mise en oeuvre d'un rétrocontrôle de la quantit?introduite du fluide supercritique sur la base d'un résultat de mesure ; et
le polyester cristal liquide a une tension ?l'état fondu ?une température supérieure de 20 °C ?la température de début d'écoulement d'au moins 5 mN mais non supérieure ? 100 mN, laquelle tension ?l'état fondu étant mesurée conformément ?la description.

2. Méthode pour produire des articles expansés moulés selon la revendication 1, dans laquelle le polyester cristal liquide a un motif de répétition représent?par la formule générale (1) indiquée ci-dessous, un motif de répétition représent?par la formule générale (2) indiquée ci-dessous, et un motif de répétition représent?par la formule générale (3) indiquée ci-dessous :

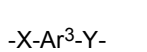
(1)



(2)



(3)



dans lesquelles

Ar^1 représente un groupe phénylène, un groupe naphtylène ou un groupe biphénylylène ;
chacun de Ar^2 et Ar^3 représente indépendamment un groupe phénylène, un groupe naphtylène, un groupe biphénylylène, ou un groupe représent?par la formule (4) indiquée ci-dessous ;
chacun de X et Y représente indépendamment un atome d'oxygène ou un groupe imino ; et
au moins un atome d'hydrogène dans Ar^1, Ar^2 et Ar^3 peut être indépendamment remplac?par un atome d'halogène, un groupe alkyle ou un groupe aryle,

(4)

dans laquelle

chacun de Ar^4 et Ar^5 représente indépendamment un groupe phénylène ou un groupe naphtylène ; et
Z représente un atome d'oxygène, un atome de soufre, un groupe carbonyle, un groupe sulfonyle ou un groupe alkylidène.

3. Méthode pour produire des articles expansés moulés selon la revendication 1 ou 2, dans laquelle, après l'injection de la composition de résine malaxée ?l'état fondu contenant le fluide supercritique dans le moule, la composition de résine contenant le fluide supercritique est expansée par utilisation d'une méthode de moulage sandwich par injection.

4. Méthode pour produire des articles expansés moulés selon l'une quelconque des revendications 1 ?3, dans laquelle le fluide supercritique est l'azote.

5. Méthode pour produire des articles expansés moulés selon l'une quelconque des revendications 1 ?4, dans laquelle la composition de résine comprend une charge inorganique en une quantit?dépassant 0 partie en masse mais non supérieure ?100 parties en masse pour 100 parties en masse du polyester cristal liquide.

6. Méthode pour produire des articles expansés moulés selon l'une quelconque des revendications 1 ?5, dans laquelle

la viscosit?de la composition de résine ?une température supérieure de 20 °C ?la température de début d'écoulement est au moins 200 Pa·s mais non supérieure ?5 000 Pa·s, dans laquelle la viscosit?est mesurée conformément ?la description.

7. Article expans?moul?qui est moul??partir d'un matériau d'expansion et d'une composition de résine, dans lequel

la composition de résine comprend un polyester cristal liquide contenant un motif de répétition représent?par la formule générale (1) indiquée ci-dessous, un motif de répétition représent?par la formule générale (2) indiquée ci-dessous, et un motif de répétition représent?par la formule générale (3) indiquée ci-dessous, et comprend également une charge inorganique,
la quantit?de la charge inorganique dépasse 0 partie en masse mais n'est pas supérieure ?100 parties en masse pour 100 parties en masse du polyester cristal liquide,

(1)

$$-O-Ar^1-CO-$$

(2)

$$-CO-Ar^2-CO-$$

(3)

$$-X-Ar^3-Y-$$

dans lesquelles

Ar^1 représente un groupe phénylène, un groupe naphtylène ou un groupe biphénylylène ;
chacun de Ar^2 et Ar^3 représente indépendamment un groupe phénylène, un groupe naphtylène, un groupe biphénylylène, ou un groupe représent?par la formule (4) indiquée ci-dessous ;
chacun de X et Y représente indépendamment un atome d'oxygène ou un groupe imino ; et
au moins un atome d'hydrogène dans Ar^1, Ar^2 et Ar^3 peut être indépendamment remplac?par un atome d'halogène, un groupe alkyle ou un groupe aryle,

(4)

$$-Ar^4-Z-Ar^5-$$

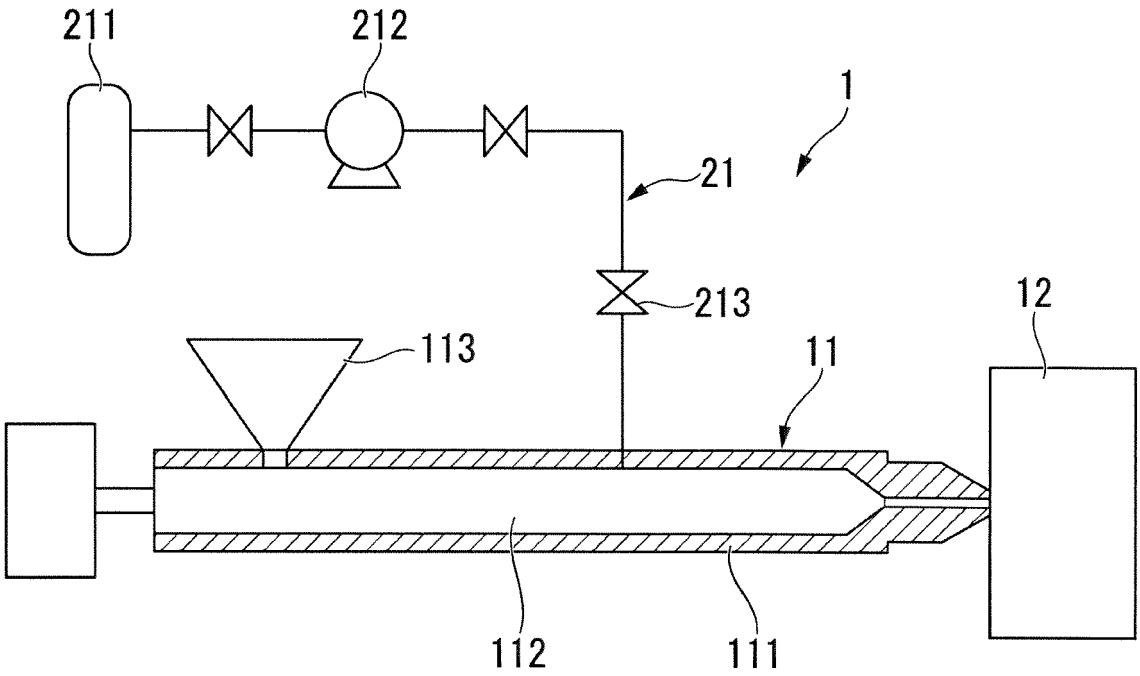
dans laquelle

chacun de Ar^4 et Ar^5 représente indépendamment un groupe phénylène ou un groupe naphtylène ; et
Z représente un atome d'oxygène, un atome de soufre, un groupe carbonyle, un groupe sulfonyle ou un groupe alkylidène ;

caractéris?en ce que
la composition de résine a une viscosit??une température supérieure de 20 °C ?la température de début d'écoulement de la composition de résine d'au moins 200 Pa.s mais non supérieure ?5 000 Pa.s, et
le polyester cristal liquide a une tension ?l'état fondu ?une température supérieure de 20 °C ?la température de début d'écoulement du polyester cristal liquide d'au moins 5 mN mais non supérieure ?100 mN,
dans lequel la viscosit?et la tension ?l'état fondu sont mesurées conformément ?la description.

8. Article expans?moul?selon la revendication 7, ayant une portion ?paroi mince avec une épaisseur de 4,0 mm ou moins.

FIG. 1



REFERENCES CITED IN THE DESCRIPTION

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